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(54) Title: HIGH MELT VISCOSITY FILLED POLYESTER COMPOSITION

(57) Abstract

Branched polyester resins comprising a polyester resin, a polyepoxy compound and a reinforcing filler having enhanced melt viscosity are disclosed.

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HIGH MELT VISCOSITY FILLED POLYESTER COMPOSITION

This is a continuation-in-part application of copending commonly assigned United States Patent Application, Serial No. 07/406,905, filed September 14, 1989, attorney's docket 336-2209 (8CV-4987).

The present invention relates to branched polyester resin compositions. More particularly the present invention relates to branched polyester resins having enhanced melt viscosity. The present invention also relates to methods for enhancing the viscosity of branched polyester resin compositions.

BACKGROUND OF THE INVENTION

Linear polyesters, such as poly(ethylene terephthalate) or PET, and poly(butylene terephthalate) or PBT, are widely used in the preparation of articles by forming methods such as injection molding. Many of their properties, including chemical stability, solvent resistance and low permeability to gases, make them attractive candidates for such forming operations as blow molding, profile extrusion and thermoforming. One problem in such operations is the relatively low melt viscosities of the polyesters, as a result of which the formed articles do not adequately retain their shape immediately after forming and before they have cooled.

In recent years, methods have been developed for increasing the melt viscosities and melt strengths of such polyesters. For example, Japanese Kokai 75/96648 and Japanese Kokai 81/116749 describe the reaction of various thermoplastic polyesters with triglycidyl isocyanurate (TGIC). In this reaction, a branched polyester is apparently formed by reaction of carboxylic acid end groups of the polyester with each of the epoxy groups. By reason of this branching, the polyester displays low viscosity at high shear rates, as during extrusion, and high viscosity and melt elasticity

at low shear rates, as during hanging of a blow-molded parison, which ensures dimensional stability.

More recently, improved methods for conducting this reaction have been developed. United States Patent Application Serial No. 185,534, filed April 21, 1988, describes the initial preparation of a reactive concentrate by the reaction of a relatively large amount of the polyepoxide with a linear polyester having a measurable proportion of free carboxylic acid end groups. The reactive concentrate is then melt blended with further linear polyester to form the desired branched polyester product. A somewhat different method, employing a concentrate in which the polymer is non-reactive with the polyepoxide, is the subject of United States Patent Application Serial No. 125,859, filed November 27, 1987. Both applications are copending and commonly owned herewith.

Kodama et al., United States Patent No. 4,141,882 describes obtaining a polyester composition having high melt viscosity by blending a polyester comprising at least 80 percent by mole of ethylene terephthalate units with (1) an epoxy compound (A) and at least one organic compound (B) capable of reacting with the epoxy compound (A), or (2) a product of the melt reaction of epoxy compound (A) with the organic compound (B).

Blaschke et al., United Kingdom Patent No. 2,098,231 describe shaped bodies formed of polytetramethylene terephthalate stabilized with TGIC. The patentees also teach the addition of hindered phenolic stabilizers to the polyester compositions.

Commonly assigned, United States Patent Application Serial No. 07/322,471, filed March 3, 1989, now allowed, discloses adding an effective amount of a catalyst compound to a polyester and polyepoxy compound composition to increase the melt viscosity of the polyester polyepoxy compound composition.

Commonly assigned copending parent application, United States Serial No. 07/406,905, filed September 14, 1989, discloses adding an effective amount of an additional catalyst compound to a polyester composition comprising a polyester resin, a polyepoxy compound, and a hindered phenolic thermal stabilizer to enhance melt viscosity and melt strength.

It has now unexpectedly been found that products with still better viscosity properties are obtained where a reinforcing mineral is added to a polyester composition comprising a polyester resin, and a polyepoxy compound. Surprisingly, the addition of the reinforcing mineral significantly enhances the melt viscosity and melt strength of polyester compositions. This also enables the producer to obtain a product resin of equivalent melt viscosity while employing less polyepoxy compound.

SUMMARY OF THE INVENTION

According to the present invention there is provided a thermoplastic resin composition comprising (a) a polyester resin; (b) a polyepoxy compound; and (c) a reinforcing mineral. Preferably the compositions further comprise (d) an additional catalyst compound or (e) a hindered phenol stabilizer, or both (d) and (e).

Preferably the polyester component (a) is selected from the group consisting of poly(1,4-butylene terephthalate), poly(ethylene terephthalate), poly(1,4-cyclohexanedimethanol terephthalate) and blends of any of the foregoing; and is present in an amount ranging from about 60 to about 90 weight percent based on the weight of the total composition.

The preferred polyepoxy compounds (b) comprise poly(O- or N-epoxyalkyl)-substituted cyclic amides, imides or imidates. Most preferred is triglycidyl isocyanurate.

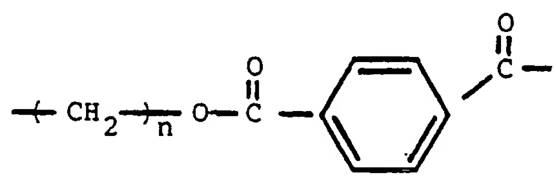
The preferred reinforcing minerals (c) are filamentous glass fibers such as E glass fibers, glass flakes and mica and are preferably present in amounts ranging from about 40 to about 10 weight percent based on the total weight of the composition.

Also according to the present invention there are provided methods for producing thermoplastic resin compositions having improved viscosity comprising: (i) melt blending a composition comprising (a) a polyester resin; and (b) a polyepoxy compound; and (ii) adding an effective amount of a reinforcing mineral; whereby either (1) the viscosity of the composition is increased over a composition comprising equivalent amounts of components (a) and (b) or (2) a composition having the same viscosity as a composition of (a) and (b) is obtained but with a reduction in the amount of (b) employed.

Further, according to the present invention there are provided methods for producing an improved thermoplastic resin composition comprising (i) melt blending (a) a relatively major amount of a polyester resin; and (b) a relatively minor amount of a polyepoxy compound; to form a resin concentrate, and (ii) adding (c) an effective amount of a reinforcing mineral and (d) an additional amount of the polyester resin (i)(a) to the resin concentrate obtained in step (i); whereby either (1) the viscosity of the composition is increased over a composition comprising equivalent amounts of (i)(a), (i)(b) and (ii)(d) or (2) the viscosity of the composition is the same and the amount of component (i)(b) employed is reduced.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

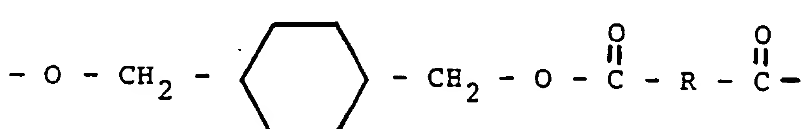
Component (a) of the present invention comprises polyester resins. Polyesters generally for use herein are derived from an aliphatic or cycloaliphatic diol, or mixtures thereof, containing from 2 to about 10 carbon atoms and at least one aromatic dicarboxylic acid. Preferred polyesters are derived from an aliphatic diol and an aromatic dicarboxylic acid and have repeating units of the following general formula:



wherein n is an integer of from 2 to 6. The most preferred polyesters are poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

Also contemplated herein are the above polyesters with minor amounts, e.g., from 0.5 to about 5 percent by weight, of units derived from aliphatic acids and/or aliphatic polyols to form copolyesters. The aliphatic polyols include glycols, such as poly(ethylene glycol). All such polyesters can be made following the teachings of, for example, U.S. Pat. No. 2,465,319 and 3,047,539.

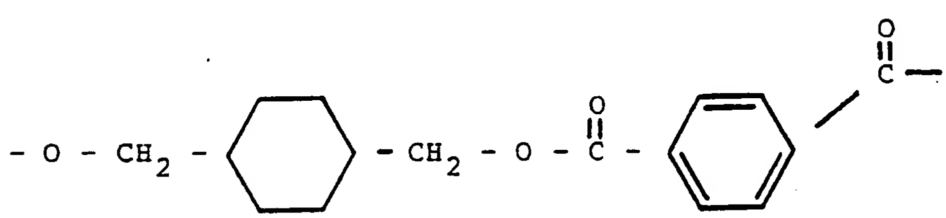
The polyesters which are derived from a cycloaliphatic diol and an aromatic dicarboxylic acid are prepared, for example, by condensing either the cis- or trans- isomer (or mixtures thereof) of, for example, 1,4-cyclohexanedimethanol with an aromatic dicarboxylic acid so as to produce a polyester having recurring units of the following formula:



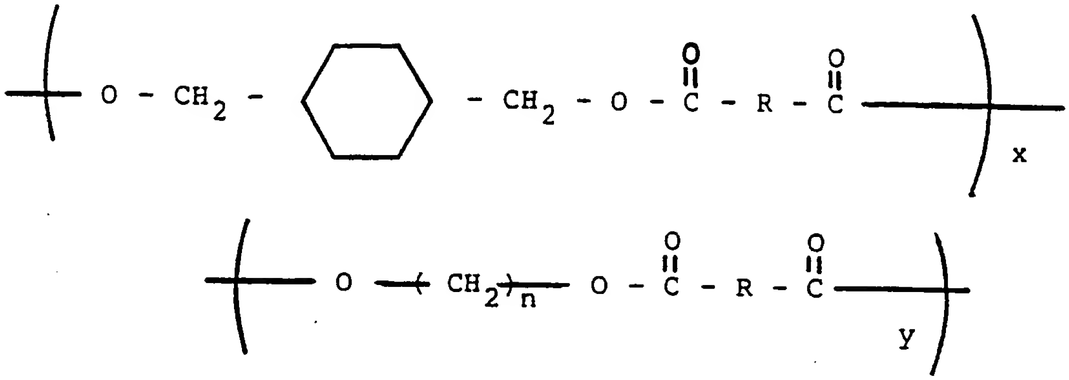
wherein the cyclohexane ring is selected from the cis- and trans- isomers thereof and R represents an aryl radical containing 6 to 20 carbon atoms and which is the decarboxylated residue derived from an aromatic dicarboxylic acid.

Examples of aromatic dicarboxylic acids represented by the decarboxylated residue R are isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, etc., and mixtures of these. All of these acids contain at least one aromatic nucleus. Acids containing fused rings can also be present, such as in 1,4- or 1,5-naphthalenedicarboxylic acids. The preferred dicarboxylic acids are terephthalic acid or a mixture of terephthalic and isophthalic acids.

Another preferred polyester may be derived from the reaction of either the cis- or trans- isomer (or a mixture thereof) of 1,4-cyclohexanedimethanol with a mixture of isophthalic and terephthalic acids. Such a polyester would have repeating units of the formula:

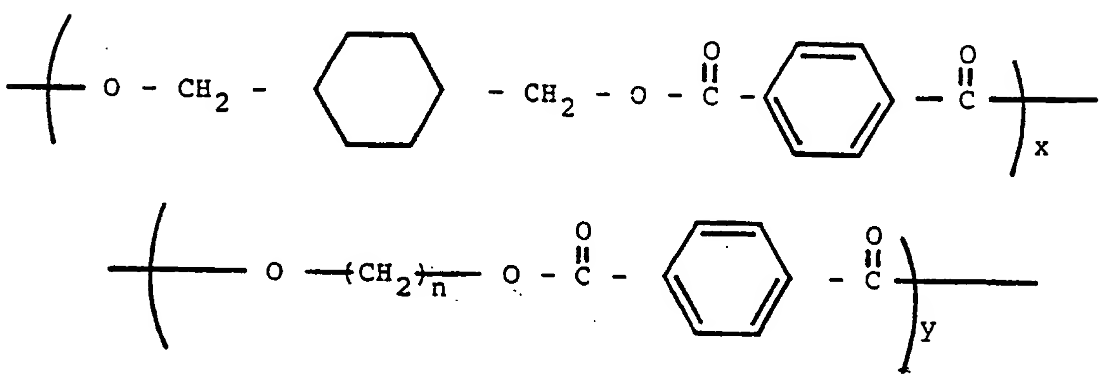


Still another preferred polyester is a copolyester derived from a cyclohexanedimethanol, an alkylene glycol and an aromatic dicarboxylic acid. These copolyesters are prepared by condensing either the cis- or trans- isomer (or mixtures thereof) of, for example, 1,4-cyclohexanedimethanol and an alkylene glycol with an aromatic dicarboxylic acid so as to produce a copolyester having units of the formulae:



wherein the cyclohexane ring is selected from the cis- and trans- isomers thereof, R is as previously defined, n is an integer of 2 to 6, the x units comprise from about 10 to about 90 percent by weight and the y units comprise from about 90 to about 10 percent by weight.

Such a preferred copolyester may be derived from the reaction of either the cis- or trans- isomer (or mixtures thereof) of 1,4-cyclohexanedimethanol and ethylene glycol with terephthalic acid in a molar ratio of 1:2:3. These copolyesters have repeating units of the following formula:



wherein x and y are as previously defined.

The polyesters described herein are either commercially available or can be produced by methods well known in the art, such as those set forth in, for example, U.S. Pat. No. 2,901,466.

The polyesters used herein have an intrinsic viscosity of from about 0.4 to about 2.0 dl/g as

measured in a 60:40 phenol/tetrachloroethane mixture or similar solvent at 23° - 30°C.

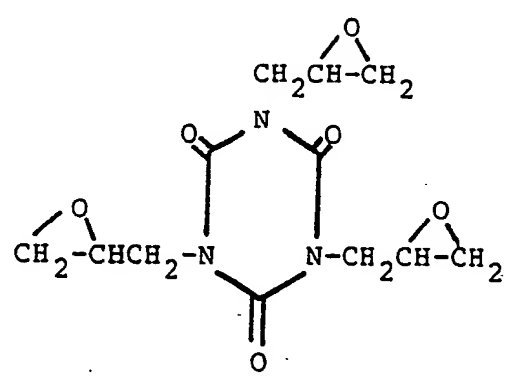
The polyester resin component can vary widely in amount. Preferably the polyester resin component is present in an amount ranging from about 60 to about 90 weight percent based on the weight of the polyester resin, polyepoxy compound, hindered phenol thermal stabilizer, additional catalyst compound and glass filler combined. Where a blend of poly(ethylene terephthalate) and poly(1,4-butylene terephthalate) is employed, the polyester resin component will comprise from about 1 to about 99 parts by weight poly(ethylene terephthalate) and from about 99 to about 1 part by weight poly(1,4-butylene terephthalate) based on 100 parts by weight of the poly(ethylene terephthalate) and poly(1,4-butylene terephthalate) combined. However, other polyester blends are also contemplated within the scope of the present invention.

Component (b) is at least one polyepoxy compound. Many types of polyepoxy compounds are known in the art and any of them are capable for use in the present invention. They include bisphenol diglycidyl ethers, epoxy novolacs, glycidyl adducts of amines and amides, glycidyl adducts of carboxylic acids, polymers of unsaturated epoxides and compounds prepared by epoxidation of dienes or polyenes. The preferred polyepoxy compounds are poly(O- or N-epoxyalkyl)-substituted cyclic amides, imides and imidates, usually containing one non-epoxy cyclic moiety although compounds with linked or fused moieties are also contemplated.

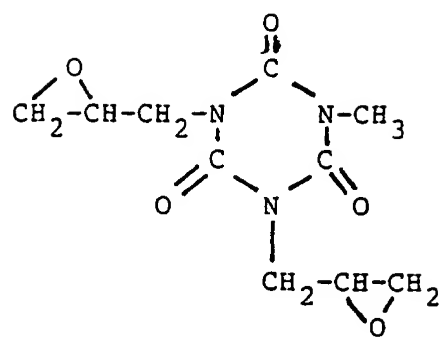
Most often, component (b) is a compound in which the epoxyalkyl groups are bonded directly to the oxygen or nitrogen atoms; however, compounds containing intervening structures, such as 2-carboglycidyloxyethyl

compounds, may also be used. The presence of more than one epoxy group per molecule is essential. At least three of such groups are highly preferred, with three being especially preferred, by reason of the ease of preparation therefrom of branched polyesters with a minimum of crosslinking and resulting gel formation.

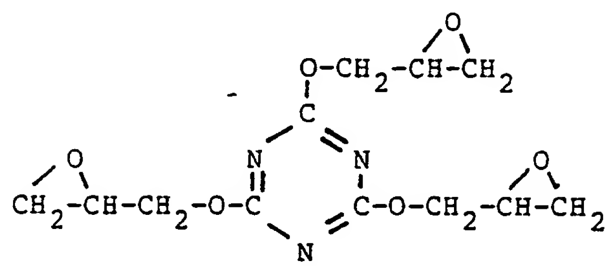
Illustrative cyclic nuclei which may be present in component (b) are the triazine, barbiturate, hydantoin, uracil, pyromellitic diimide, piperazinedione and parabanate ring system. As previously noted, the epoxy containing functionalities may be present as substituents on oxygen or nitrogen atoms therein, with nitrogen atoms frequently being preferred. The most suitable compounds are triazine derivatives, including triglycidyl cyanurate and TGIC. TGIC is particularly preferred by reason of its availability and particular suitability for the formation of branched polyesters. It has the formula



Other suitable triazine derivatives or N-methyl-N', N"-diglycidyl isocyanurate of the formula



and triglycidyl cyanurate of the formula



Essential to the compositions of the present invention is component (c) a reinforcing mineral. Preferably the reinforcing mineral is a glass filler such as filamentous glass fibers or glass flakes. These are well known to those skilled in the art and are widely available from a number of manufacturers. For compositions ultimately to be employed for electrical uses, it is prefered to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively sodium free. This is known as "E" glass. However, other glass compositions are useful. Especially preferred "E" glasses are K filament glass (about 14 micron diameter), G filament glass (about 10 micron diameter) and D filament glass (about 7 micron diameter). All such glasses are contemplated as within the scope of the present invention. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing

and mechanical pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters preferably range from about 0.00012 to about 0.00075 inch, but this is not critical to the present invention. It is known, however, to those skilled in the art, that smaller filament diameters will also increase the strength of plastics treated therewith.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, or woven into mats, and the like are also not critical to the invention. However, in preparing the molding compositions of the present invention, it is convenient to use filamentous glass in the form of chopped strands of from about one-eighth to about 2 inches long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur.

Other preferred reinforcing minerals are mica, asbestos, wollastonite, clay, talc, carbon, ceramic, titanate, and mixtures thereof. Talc is especially preferred.

Optional component (d) is an additional catalyst component for the polyester-polyepoxy compound reaction. Suitable catalysts are in two classes, the first of which consists of primary alkylamines in which the alkyl group contains at least about 8 and preferably about 10-20 carbon atoms. Illustrative amines of this type include octylamine, decylamine, dodecylamine, tetradecylamine, pentadecylamine and eicosylamine. Included is the use of mixtures containing such amines, some of which are commercially available as accelerators for crosslinking of polyepoxy compounds. For example, the mixture of a long chain amine, a long chain

quaternary ammonium salt and stannous octoate in a polymeric medium sold by Ciba-Geigy under the designation "XB3126" is suitable for use as a catalyst.

The second class of catalytic compounds consist of salts free from direct carbon-phosphorus bonds and containing at least one of alkali and alkaline earth metal cations and halide anions. It is apparent that this class contains a large number of compounds. They include alkali metal halides, alkali metal carboxylates, alkali metal enolates, amine hydrohalides and quaternary ammonium halides. Illustrative compounds within this class are lithium fluoride, lithium iodide, potassium bromide, sodium dihydrogen phosphate, sodium acetate, sodium benzoate, sodium caproate, sodium stearate, sodium ascorbate and dodecyltrimethylammonium bromide.

At high temperatures, as under melt conditions, thermoplastic polyesters undergo hydrolysis and molecular weight degradation by traces of water. Therefore, it is highly preferred for the catalyst to be free from substantial quantities of water. In general, water proportions greater than those present in a monohydrate of the catalyst should be avoided. It is generally advisable to employ anhydrous and/or non-hygroscopic salts as catalysts.

Salts of aliphatic carboxylic acids containing at least about 18 carbon atoms, especially the alkali metal stearates and preferably sodium stearate, have certain advantages over the other catalysts employed according to the invention and are therefore often preferred. In the first place, their use permits extrusion of the polyester-polyepoxide composition at substantially higher feed rates than those which are effective in their absence. In the second place, they tend to suppress the formation of acrolein, a by-product

from glycidyl reagents such as TGIC. In the third place, they impart substantially less odor to the composition than certain other compounds useful as catalysts, especially amines.

Optional component (e) of the present invention comprises a hindered phenol thermal stabilizer. Any hindered phenol known to those skilled in the art may be employed herein, a wide variety of these are commercially available.

Hindered phenols will generally be of the type in which there is a sterically hindered phenolic group, especially one containing a t-butyl group in the oposition to the phenolic OHgroup. Examples of such compounds are many. Preferred examples are, tetrakis (methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate)methane; octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl)benzene; 4,4'-(2,2-diphenylpropyl)diphenylamine; esters of ethoxylated aryl phenols; 2,2'-thiodiethylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl))propionate; octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate and mixtures of any of the foregoing. Most preferred is octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate, which is commercially available as "IRGANOX" 1076.

The proportion of polyepoxy compound employed according to the present invention is generally about 0.05 - 3.0 parts by weight per 100 parts of polyester. The catalyst is employed in an amount ranging in general from about 0.01 to about 0.5 parts per 100 parts of polyester. For alkali metal stearates, about 0.01 - 0.20 parts is preferred. Preferably, the glass filler is present in an amount of at least about 10 parts by weight per 100 parts by weight of the total composition, more preferably at least about 20 parts by weight.

The invention requires effecting reaction between the polyester and polyepoxy compound in the presence of the catalyst to form a branched polyester resin. Conventional blending methods may be used to effect the reaction. Melt blending methods are typically employed, frequently preceded by a dry blending step. A melt blending operation which is often preferred is extrusion, ordinarily at temperatures in the range of about 200 - 300°C. Any conventional extruder known to those skilled in the art may be employed.

TGIC and similar compounds are typically supplied as powders which may agglomerate into coarse particles. These particles are frequently difficult to mix uniformly with the other components during extrusion, and may result in regions of gel formation which produce flaw sites in formed articles. Moreover, many such compounds could be irritants and/or health hazards.

For this reason, it is frequently preferred to initially prepare a concentrate by blending a relatively large amount of the polyepoxide with the polyester. Concentrates of this type may be prepared by melt blending or solution blending techniques as appropriate, and typically contain about 3 - 20 parts by weight of polyepoxide per 100 parts of polyester.

The concentrates thus prepared are essentially indistinguishable in appearance and physical behavior from the resin used for their preparation. No obvious indicia of phase separation are observed therein. The concentrate is dust-free and should be handled with minimum skin contact and inhalation of the polyepoxide. It may be readily pelletized for easy handling. By the preparation of (for example) one batch of such a concentrate, continued or repeated handling of

polyepoxide is made unnecessary. Reference is again made to the aforementioned copending applications Serial Nos. 125,859 and 184,534 for further details of the preparation of branched polyester compositions using concentrates.

When such concentrates are employed, the additional catalyst, antioxidant and reinforcing mineral may be incorporated in the mixture at the time of preparation of the concentrate and/or when the concentrate is subsequently blended with further polyester. Subsequent blending of glass filler is often especially preferred.

The compositions of the present invention can also comprise any number of conventional additives, such as dyes, pigments, stabilizers, plasticizers, flame retardants, drip retardants, nucleants, rubbery impact modifiers and the like. These are added, as desired, for their conventionally employed purposes. Illustrative flame retardant additives are disclosed in United States Patent Nos. 3,833,685; 3,341,154; 3,915,926 and 3,671,487. Other flame retardants are disclosed in United States Patent Nos. 3,681,281; 3,557,053; 3,830,771 and United Kingdom Patent No. 1,358,080.

Generally speaking, the more important of the flame retardant compounds contain chemical elements employed for their ability to impart flame resistance, e.g., bromine, chlorine, antimony, phosphorous and nitrogen. It is preferred that the flame-retardant additive comprise a halogenated organic compound (brominated or chlorinated); a halogenated-containing organic compound in admixture with a phosphorous compound or compounds containing phosphorous-nitrogen bonds or a mixture of two or more of the foregoing.

The amount of flame retardant additive used is not critical to the present invention, so long as it is

present in a minor proportion based on said composition, major proportions will detract from physical properties, but at least sufficient to render the polyester resin non-burning or self-extinguishing. Those skilled in the art are well aware that the amount will vary with the nature of the resin and with the efficiency of the additive. In general, however, the amount of additive will be from 0.5 to 50 parts by weight per 100 parts of resin.

A preferred range will be from about 3 to 25 parts and an especially preferred range will be from about 8 to 12 parts of flame retardant additive per 100 parts of resin. Smaller amounts of compounds highly concentrated in the elements responsible for flame-retardance will be sufficient, e.g. elemental red phosphorous will be preferred at 0.5 to 2.0 parts by weight per hundred parts of resin, while phosphorous in the form of triphenyl phosphate will be used at 25 parts of phosphate per 100 parts of resin, and so forth. Halogenated aromatics will be used at 8 to 12 parts and synergists, e.g., antimony oxide, will be used at about 2 to 5 parts by weight per 100 parts of resin.

The preferred halogen compounds for this invention are aromatic halogen compounds such as brominated phthalimides, brominated polystyrene, brominated aryl ethers, halogenated bisphenols, polycarbonate polymers of halogenated bisphenols, brominated biphenyl, brominated terphenyl, or a compound comprising two phenyl radicals separated by a divalent alkylene or oxygen group and having at least two chlorine or bromine atoms per phenyl nucleus, and mixtures of at least two of the foregoing. Especially preferred are brominated phthalimides and polycarbonate oligomers of brominated bisphenols, alone, or mixed with antimony oxide.

In general, the preferred phosphate compounds are selected from elemental phosphorous or organic phosphonic acids, phosphonates, phosphinates, phosphonites, phosphinites, phosphene oxides, phosphenes, phosphites or phosphates. Illustrative is triphenyl phosphene oxide. This can be used alone, or mixed with brominated phthalimides or halogenated polycarbonates and, optionally, antimony oxide.

The compositions of the present invention may also comprise a drip retardant agent. These are described in U.S. Patent No. 3,671,487. Generally, the drip retardant agent comprises a polytetrafluoroethylene resin, which is commercially available or can be prepared by known processes. They are white solids obtained by polymerization of the tetrafluoroethylene in aqueous media with free radical catalysts, e.g., sodium, potassium or ammonium peroxydisulfates at 100 to 1,000 psi and at 0-200°C and preferably 200 - 100°C. See Brubaker, United States Patent No. 2,393,967.

The compositions of the present invention may then be formed into articles. Preferably the compounded resin is extruded into a sheet and then thermoformed into a variety of articles. The compositions are also suitable for profile extrusion, blow molding and other processes known to those skilled in the art that require higher melt strength than normal systems. See, e.g., Modern Plastics Encyclopedia '89, McGraw Hill, Vol. 65, No. 11, pp. 215-308.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following specific examples illustrate the present invention. However, they are not to be construed to limit the claims in any manner whatsoever.

EXAMPLES 1 - 2

Reactively branched poly(1,4-butylene terephthalate)(RBPBT) is prepared by combining 94.05

weight percent "VALOX" 315 PBT (General Electric Company), 5.7 weight percent reactive PBT concentrate (RBC) (3.5 weight percent TGIC reacted with "VALOX" 315), 0.05 weight percent sodium stearate and 0.2 weight percent "IRGANOX" 1076 (Ciba Geigy Company). To 80 weight percent and 70 weight percent of RBPBT is added 20 weight percent and 30 weight percent of K-glass fiber (OCF-408BC), respectively, in a 2.5 inch single screw extruder and compounded at 110 rpm and at a barrel set temperature of 480°F. The extrudate is then tested for melt viscosity. In all examples melt viscosity is measured on a Tinius Olsen melt indexer at 482°F using a 0.0825 inch orifice with a 4900 gram load. The results along with compositional data are set forth below in Table 1.

TABLE 1

EXAMPLE	1	2
Composition (wt %)		
RBPBT	80	70
K-glass Fiber	20	30
% TGIC of PBT	0.20	0.20
% TGIC of blend	0.16	0.14
Property		
Melt viscosity at 482°F, poise	25,800	25,900

It can be seen from Table 1 above that the compositions of the present invention possess excellent melt viscosity characteristics.

EXAMPLES 3 - 6

The procedure of Example 1 is followed except the amounts of PBT, RBC and glass fiber are varied. A comparison is also made with a sample having no glass fiber. The results along with compositional data are set forth below in Table 2.

TABLE 2

Example	3A*	3	4	5	6
Composition (wt%)					
PBT[a]	94.45	85.85	76.35	71.55	66.75
RBC[b]	4.3	3.9	3.4	3.2	3.0
Irganox® 1076[c]	0.2	0.2	0.2	0.2	0.2
NaStearate	0.05	0.05	0.05	0.05	0.05
Glass Fiber[d]	-	10.0	20.0	25.0	30.0
% TGIC of PBT	0.15	0.15	0.15	0.15	0.15
% of TGIC of blend	0.15	0.137	0.119	0.112	0.105
Property					
Melt Viscosity at 482°F poise	55,400	No Flow	64,800	82,400	82,400

* = Comparative Example
a = Valox® 315 resin, General Electric Plastics
b = extruded concentrate of Valox® 315 PBT resin with 3.5 weight percent TGIC
c = hindered phenol antioxidant, Ciba Geigy Company
d = OCF-408BC chopped glass fibers, Owens Corning Fiberglass

It can be seen from Table 2 above the excellent improvement in melt viscosity in polyester resins having K-glass fibers compared to those with no glass fibers.

EXAMPLES 7 - 9

The procedure of Example 1 is followed except the TGIC concentration in the PBT resin is varied. The results along with compositional data are set forth below in Table 3.

TABLE 3

Example	7A*	7	8	9
Composition (wt %)				
PBT[a]	69.75	68.75	68.25	67.75
RBC[b]	-	1.00	1.50	2.00
Irganox® 1076[c]	0.05	0.05	0.05	0.05
NaStearate	0.20	0.20	0.20	0.20
GF[d]	30.00	30.00	30.00	30.00
% TGIC	0.0	0.035	0.053	0.07
Property				
Melt Viscosity at 482°F, poise	32,700	43,600	46,600	56,100

* = Comparative Example
a = Valox® 315 resin, General Electric Plastics
b = extruded concentrate of Valox® 315 PBT resin with 3.5 weight percent of TGIC
c = hindered phenol antioxidant, Ciba Geigy Company
d = OCF 408BC chopped glass fibers, Owens Corning Fiberglass

Table 3 above demonstrates the excellent improvement in the viscosity of polyester resins obtained by the addition OCF-408BC chopped glass fibers as the reinforcing mineral and varying TGIC concentrations.

EXAMPLES 10 - 11

The procedure of Example 1 is followed except clay is employed as the reinforcing mineral instead of glass fibers. The results along with compositional data are set forth below in Table 4.

TABLE 4

EXAMPLE	10	11
Composition (wt %)		
RBT[a]	76.35	71.55
RBC[b]	3.4	3.2
Irganox® 1076[c]	0.2	0.2
NaStearate	0.05	0.05
Clay[d]	20.0	25.0
% TGIC	0.119	0.112
Property		
Melt Viscosity at 482°F, poise	18,600	26,300

a = Valox® 315 resin, General Electric Plastics
b = extruded concentrate of Valox® 315 PBT resin with 3.5 weight percent TGIC
c = hindered phenol antioxidant, Ciba Geigy Company
d = Translink 445, Engelhard Company

Table 4 above demonstrates that polyester resins having improved viscosity are obtained where clay is employed as the reinforcing mineral.

EXAMPLES 12 - 14

The procedure of Example 1 is followed except mica is employed as the reinforcing mineral. The results along with compositional data are set forth below in Table 5.

TABLE 5

EXAMPLE	12A*	12	13	14
Composition (wt%)				
PBT[a]	95.45	76.35	71.55	70.55
RBC[b]	4.3	3.4	3.2	3.2
Irganox® 1076[c]	0.2	0.2	0.2	0.2
NaStearate	0.05	0.05	0.05	0.05
Mica[d]	-	20.0	25.0	25.0
TiO_2	-	-	-	1.0
% TGIC	0.151	0.119	0.112	0.112
Property				
Melt Viscosity at 482°F, poise	30,700	33,800	47,900	61,900

* = Comparative Example
a = Valox® 315 resin, General Electric Plastics
b = extruded concentrate of Valox® 315 PBT resin with 3.5 weight percent TGIC
c = hindered phenol antioxidant, Ciba Geigy Company
d = Suzorite Mica 150S

Table 5 above shows the improvement to polyester resin melt viscosity provided by mica as the reinforcing mineral.

EXAMPLES 15 - 16

The procedure of Example 1 is followed except talc is employed as the reinforcing mineral. The results along with compositional data are set forth below in Table 6.

TABLE 6

EXAMPLE	15	16
Composition (wt %)		
PBT[a]	75.25	65.84
RBC[b]	4.55	3.99
Irganox® 1076[c]	0.16	0.14
NaStearate	0.04	0.03
Talc[d]	20.0	30.0
% TGIC	0.159	0.140
Property		
Melt Viscosity at 482°F, poise	25,800	25,900

a = Valox® 315 resin, General Electric Plastics
b = extruded concentrate of Valox® 315 PBT resin with 3.5 weight percent TGIC
c = hindered phenol antioxidant, Ciba Geigy Company
d = Talcron NP 45-26, Pfizer Company

Table 6 above demonstrates the improved melt viscosity of polyester resins wherein talc is employed as the reinforcing mineral.

The above mentioned patents and patent applications are all hereby incorporated by reference.

Many variations of the present invention will suggest themselves to those skilled in this art in light of the above detailed description. For example, instead of poly(1,4-butylene terephthalate), other polyester resins such as a poly(ethylene terephthalate), a poly(1,4-cylcohexanedimethyl terephthalate) or mixtures thereof may be employed. Additionally, a number of polyepoxide compounds may be used, e.g., a bisphenol diglycidyl ether, an epoxy novolac, N-methyl-N',N"-diglycidyl isocyanurate, and triglycidyl cyanurate. Further, instead of filamentous glass fibers; glass flakes, mica, titanates, asbestos, wollastonite, clay

talc, carbon, ceramic and mixtures of any of the foregoing may be employed as the reinforcing mineral. A number of hindered phenols are also contemplated for use herein in addition to "IRGANOX" 1076. These include esters of ethoxylated aryl phenols, tetrakis(methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate) methane, octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene; 4,4'-(2,2-phenylpropyl) diphenylamine, and 2,2'-thiodiethylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl))propionate. Also contemplated for use herein as an additional catalyst compound are potassium bromide, lithium iodíde, lithium fluoride, sodium acetate, sodium caproate, sodium benzoate, sodium ascorbate, sodium dihydrogen phosphate, dodecyltrimethylammonium bromide and mixtures thereof. Flame retardants, such as a brominated polycarbonate or brominated phthalimide in admixture with antimony oxide; and drip retardants may also be added to the compositions of the present invention. All such obvious modifications are within the full intended scope of the appended claims.

CLAIMS

1. A thermoplastic resin composition comprising:

(a) a polyester resin;

(b) a polyepoxy compound; and

(c) a reinforcing mineral.

2. A composition as defined in Claim 1 wherein said component (a) polyester resin comprises units of an aliphatic diol, a cycloaliphatic diol or a mixture of such diols and an aromatic diacid.

3. A composition as defined in Claim 2 wherein said component (a) polyester resin is selected from the group consisting of a poly(1,4-butylene terephthalate), poly(ethylene terephthalate), poly(1,4-cyclohexanedimethyl terephthalate) and blends of any of the foregoing.

4. A composition as defined in Claim 1 wherein said component (a) polyester resin has an intrinsic viscosity of at least about 0.4 deciliters per gram when measured in a 60:40 mixture of phenol and trichloroethane at 30°C.

5. A composition as defined in Claim 1 wherein said component (b) polyepoxy compound comprises a poly(O- or N-epoxyalkyl)-substituted cyclic amide, imide or imidate.

6. A composition as defined in Claim 5 wherein said polyepoxy compound comprises a single triazine, barbiturate, hydantoin, uracil, pyromellitic diimide, piperazinedione or parabanate group and the epoxyalkyl groups therein are bonded directly to oxygen or nitrogen atoms.

7. A composition as defined in Claim 6 wherein said polyepoxy compound is selected from the group consisting of triglycidyl isocyanurate, N-methyl-N',N"-diglycidylisocyanurate, triglycidyl cyanurate and a mixture of any of the foregoing.

8. A composition as defined in Claim 7 wherein said polyepoxy compound comprises triglycidyl isocyanurate.

9. A composition as defined in Claim 1 wherein said component (c) reinforcing mineral is selected from the group consisting of glass fibers, glass flakes, mica and mixtures of any of the foregoing.

10. A composition as defined in Claim 9 wherein said component (c) reinforcing mineral comprises glass fibers.

11. A composition as defined in Claim 1 which further comprises (d) an additional catalyst compound.

12. A composition as defined in Claim 11 wherein said component (d) additional catalyst compound is selected from the group consisting of (1) primary alkylamines in which the alkyl group contains at least about 8 carbon atoms and (2) salts free from direct carbon-phosphorous bonds and containing at least one of alkali and alkaline earth metal cations and halide anions.

13. A composition as defined in Claim 12 wherein said catalyst compound comprises a primary alkylamine containing about 10 to 20 carbon atoms.

14. A composition as defined in Claim 13 wherein said catalyst compound is selected from the group consisting of potassium bromide, lithium iodide, lithium fluoride, sodium acetate, sodium caproate, sodium benzoate, sodium stearate, sodium ascorbate, sodium dihydrogen phosphate, dodecyltrimethylammonium bromide and mixtures thereof.

15. A composition as defined in Claim 14 wherein said catalyst compound comprises sodium stearate.

16. A composition as defined in Claim 1 which further comprises component (e) a hindered phenol thermal stabilizer.

17. A composition as defined in Claim 1 wherein said composition comprises at least about 0.05 parts by weight of said polyepoxy compound component (b) and at least about 10 parts by weight of said reinforcing mineral component (c) based on 100 parts by weight of the total composition.

18. A composition as defined in Claim 17 wherein said composition comprises at least about 20 parts by weight of said reinforcing mineral component (c).

19. A composition as defined in Claim 1 which further comprises (f) an effective amount of a flame retardant agent.

20. A composition as defined in Claim 1 wherein said composition also comprises (g) a drip retardant agent.

21. A method for producing a thermoplastic resin composition having improved viscosity comprising:

(i) melt blending a composition comprising:

(a) a polyester resin;

(b) a polyepoxy compound; and

(ii) adding an effective amount of (c) a reinforcing mineral; whereby either (1) the viscosity of the composition is increased over a composition comprising equivalent amounts of components (a) and (b) or (2) a composition having the same viscosity as a composition of (a) and (b) is obtained but with a reduction in the amount of (b) employed.

22. A method as defined in Claim 21 wherein said component (a) polyester resin comprises units of an aliphatic diol, a cycloaliphatic diol or a mixture of such diols and an aromatic diacid.

23. A method as defined in Claim 22 wherein said component (a) polyester resin is selected from the group consisting of poly(1,4-butylene terephthalate), poly(ethylene terephthalate), a poly(1,4-cyclohexane-dimethyl terephthalate), and blends of any of the foregoing.

24. A method as defined in Claim 21 wherein said component (a) polyester resin has an intrinsic viscosity of at least about 0.4 deciliters per gram when measured in a 60:40 mixture of phenol and trichloroethane at 30°C.

25. A method as defined in Claim 21 wherein said polyepoxy compound (b) comprises a poly(O- or N-epoxyalkyl)-substituted cyclic amide, imide or imidate.

26. A method as defined in Claim 25 wherein said polyepoxy compound comprises a single triazine, barbiturate, hydantoin, uracil, pyromellitic diimide, piperazinedione or parabanate group and the epoxyalkyl groups therein are bonded directly to oxygen or nitrogen atoms.

27. A method as defined in Claim 26 wherein said polyepoxy compound is selected from the group consisting of triglycidyl isocyanurate, N-methyl-N',N"-diglycidyl isocyanurate, triglycidyl cyanurate and mixtures of any of the foregoing.

28. A method as defined in Claim 27 wherein said polyepoxy compound comprises triglycidyl isocyanurate.

29. A method as defined in Claim 21 wherein said component (c) reinforcing mineral is selected from the group consisting of glass fibers, glass flakes, mica and mixtures of any of the foregoing.

30. A method as defined in Claim 29 wherein said component (c) reinforcing mineral comprises glass fibers.

31. A method as defined in Claim 21 which further comprises adding (d) an effective amount of an additional catalyst compound in step (i).

32. A method as defined in Claim 31 wherein said catalyst compound (d) is selected from the group consisting of (1) primary alkylamines in which the alkyl group contains at least about 8 carbon atoms and (2) salts free from direct carbon-phosphorous bonds and containing at least one of alkali and alkaline earth metal cations and halide anions.

33. A method as defined in Claim 32 wherein said catalyst compound is selected from the group consisting of potassium bromide, lithium iodide, lithium fluoride, sodium acetate, sodium caproate, sodium benzoate, sodium stearate, sodium ascorbate, sodium dihydrogen phosphate, dodecyltrimethylammonium bromide and mixtures thereof.

34. A method as defined in Claim 33 wherein said catalyst compound comprises sodium stearate.

35. A method as defined in Claim 21 wherein said composition comprises at least about 0.05 parts by weight of said polyepoxy compound component (b) and at least about 10 parts by weight of said reinforcing mineral component (c) based on 100 parts by weight of the total composition.

36. A method as defined in Claim 35 wherein said composition comprises at least about 20 parts by weight of said reinforcing mineral component (c).

37. A method as defined in Claim 21 wherein said method is carried out in an extruder.

38. A method as defined in Claim 23 which further comprises adding an effective amount of (f) a flame retardant agent in step (i).

39. A method as defined in Claim 21 which further comprises adding an effective amount of (g) a drip retardant agent in step (i).

40. A method for producing an improved thermoplastic resin composition comprising

(i) melt blending

(a) a relatively major amount of a polyester resin; and

(b) a relatively minor amount of a polyepoxy compound; to form a resin concentrate, and

(ii) adding

(c) an effective amount of reinforcing filler; and

(d) an additional amount of said polyester resin (i)(a) to the resin concentrate obtained in step (i); whereby either (1) the viscosity of the composition is increased over a composition comprising equivalent amounts of (i)(a), (i)(b), and (ii)(d); or (2) the viscosity of the composition is the same and the amount of component (i)(b) employed is reduced.

41. A method as defined in Claim 40 wherein component (ii)(c) is added in step (i).

42. A method as defined in Claim 41 wherein said resin concentrate comprises said polyepoxy compound in an amount ranging from about 1.0 to about 4.0 weight percent based on the total weight of said resin concentrate.

43. A method as defined in Claim 40 which further comprises adding (e) an additional catalyst, (f) a hindered phenol stabilizer, or (e) and (f); in either step (i) or step (ii).

44. An article comprising a thermoplastic resin composition as defined in Claim 1.

45. An article as defined in Claim 44 comprising an extruded sheet.

46. An article as defined in Claim 45 comprising a thermoformed extruded sheet.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/06095

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 67/02, C 08 L 63/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	Dialog Information Services, File 350, WPI 63-80, Dialog accession no. 002064078, WPI accession no. 78-77145A/43, Mitsubishi Chem Ind KK: "Glass fibre reinforced polyester resin compsn. - contg. polybutylene-or polypropylene terephthalate used esp. for injection moulding", JP 53106750, A, 780918, 7843 (Basic) --	1-4
Y	US, A, 4999388 (OKAMOTO) 12 March 1991, see the whole document --	1-46
Y	EP, A2, 0387565 (GENERAL ELECTRIC COMPANY) 19 September 1990, see the whole document --	1-46

* Special categories of cited documents:[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23rd April 1992	11. 05. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Danielle van der Haas

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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/06095

SA 51381

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/02/92
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For more details about this annex : see Official Journal of the European patent Office, No. 12/82

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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Y	GB, A, 2098231 (DYNAMIT NOBEL AKTIENGESELLSCHAFT) 17 November 1982, see the whole document --	1-46
Y	US, A, 4141882 (KODAMA ET AL) 27 February 1979, see the whole document --	1-46
A	EP, A1, 0423505 (GENERAL ELECTRIC COMPANY) 24 April 1991, see the whole document --	1-46
A	WO, A1, 8808597 (GENERAL ELECTRIC COMPANY) 3 November 1988, see the whole document --	1-46
E,X	Dialog Information Services, File 351, WPI 81-92, Dialog accession no. 008922289, WPI accession no. 92-049558/07, Curry H L et al: "High melt viscosity filled polyester compsns. - has melt viscosity enhances by a reinforcing material and comprises polyester resin and a polyepoxy cpd.", CA 2039838, A, 911122, 9207 (Basic) -- --------	1-46